

CHAPTER-2

LITERATURE REVIEW

## 2.0 Introduction

The present thesis embodies the results on the polymerization of methyl methacrylate (MMA), a vinyl monomer using benzoyl peroxide ( $Bz_2O_2$ ) in combination with some selected dyes or dye-intermediates having aromatic amine moieties in their structures as initiator systems. It is therefore worthwhile to review the literature at this stage covering the use of dyes or dye/intermediates as initiators # of polymerization in aqueous or non-aqueous media under thermal or photoconditions.

The review would cover systems where a dye is used as such or in combination with some other agents as the initiator systems. Keeping in view that all the initiator systems used in the present investigation contain combination of  $Bz_2O_2$  and a dye or dye-intermediate having aromatic amine moieties in their structures, peroxide-amine initiated polymerizations are also kept within the perview of this survey.

### 2.1 Dye-sensitized polymerization

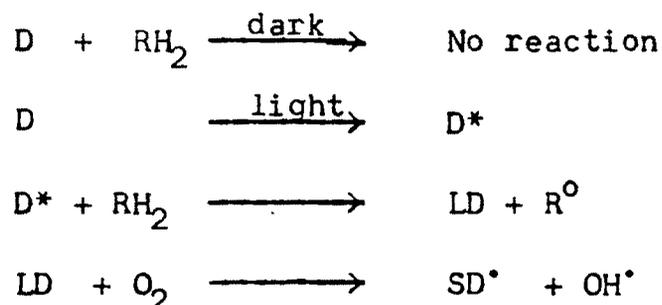
Dye sensitized photopolymerization of styrene was first reported by Bamford and Dewar<sup>42,43</sup> and since then numerous research papers have been published till recently by different workers<sup>44-120</sup> on this topic covering different monomers and different dyes and additives.

From the findings of the investigators it is apparent

that oxygen plays a vital role in ascertaining the mechanisms and kinetics of dye sensitized photopolymerization although there are contradictory views relating to the essentiality of the presence of oxygen in dye-sensitized photopolymerization of vinyl monomers and as a consequence, on the overall mechanism of sensitization, energy transfer and radical generation.

### 2.1.1 Polymerization in the presence of oxygen

The sensitizing systems in aqueous photopolymerization described by Oster<sup>44-47</sup> comprised of a photoreducible dye such as riboflavine, fluorescein, methylene blue etc. and a weak reducing agent such as triethanolamine. An appropriate amount of oxygen was considered to be essential for the radical generation process leading to initiation of polymerization of such monomers as acrylamide. The suggested mechanism is that the selected dye undergoes photoactivation to the leuco-base form which gets subsequently oxidised to free radicals by the air or oxygen present<sup>48-50</sup>.



where D and D\* represent the dye and the photo-excited dye, RH<sub>2</sub> = reducing agent, LD = leuco form of dye and R<sup>o</sup> = oxidised form of the reductant used.

The in situ formation of  $H_2O_2$  by the reoxidation of the dye have been suggested<sup>51-54</sup> and confirmed experimentally<sup>55</sup> and in fact oxygen could be substituted by  $H_2O_2$  to produce comparable effects<sup>56</sup>.  $H_2O_2$  formed or used and the reducing agent present form a redox initiating system and the interaction between them is the primary, major if not the only cause of radical generation leading to chain initiation in acrylamide polymerization. An almost identical mechanism was confirmed to be applicable to ethyl eosin sensitized photopolymerization of vinyl monomer in the presence of ascorbic acid as a reducing agent and in contamination of oxygen or air<sup>57</sup>.

Needles<sup>58-65</sup> supported this view of  $H_2O_2$  formation in his studies of photoinduced dye sensitized graft copolymerization of some acrylic monomers on substrates such as silk, wool and related fibres using riboflavin, fluorescein and anthraquinone dyes.

#### Participation of monomer in radical formation reaction

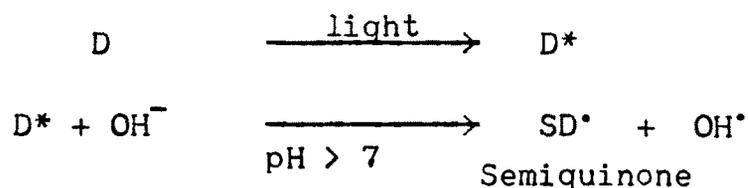
The dependence of the rate of polymerization of both acrylamide and methacrylic acid on the square of the monomer concentration as observed by Oster<sup>48</sup> and Delzenne<sup>51,52</sup> has been explained on the basis of participation of the monomer in the formation of the initiating radicals assuming a low initiating efficiency of the radicals<sup>66</sup>. This concept of radical generation by the interaction of triplet state of the dye molecules with monomer molecules was later supported by Takemura<sup>67</sup>.

Action of Cobalt (II) complexes on the dye sensitized polymerization

Addition of cobalt (II) ion in the form of complexes with triethylenetetramine, diethylene triamine, glycyglycine and histidine to the aqueous acrylamide-methylene blue system was reported to enhance the rate of photopolymerization and overall monomer conversion. Here the cobalt ion forms a reversible carrier with the electron donor (legand) and thus serves as an oxygen buffer. It was demonstrated that oxygen was essential for the chain initiation<sup>68</sup>.

2.1.2 Polymerization in the absence of oxygen

Shepp et al.<sup>69</sup> observed that with aqueous acrylamide-thionin system, a reducing agent was not necessary if oxygen was carefully excluded from the system. The proposed mechanism for the formation of free radicals is :



This mechanism was cited on the basis of the observation that polymerization occurs only at a pH > 7. The OH<sup>-</sup> ions in the aqueous alkaline medium act as reducing agents which interact with the photoexcited dye molecules leading to the formation of radicals for chain initiation.

Using a different dye (methylene blue), the above mechanism was later supported by Hsia Chen<sup>70</sup> and it was



zation with thionine dye<sup>72-74</sup>.

Investigations on the non-aqueous photopolymerization of styrene using pinacyanol iodide, azine type dyes (neutral red), cyanine and triphenyl methane type dyes revealed that polymerization took place through radical (activated) intermediates formed by direct photodecomposition of the sensitizer without the requirement of energy transfer by the sensitizer to any other species in the system prior to radical generation<sup>75,76</sup>. The excited dyes are shown to breakdown into radicals, often through interaction with the monomer<sup>77-80</sup>.

In the studies of aqueous photopolymerization of acrylamide using methylene blue-triethanolamine system, monomeric form of the cationic dye, methylene blue was found to act as an efficient sensitizer whereas its associated form was observed to be a chain terminator. A combination of methylene blue and a doubly charged anionic dye eosin Y gives rise to increased rate of polymerization and quantum yield due to the formation of a new species resulting from ionic interaction between the two dyes. The exact structure of the new ionic species, however could not be established. Methylene blue in combination with another cationic dye, acridine orange had no effect on the rate of polymerization due to practically lack of interaction between the two cationic dyes<sup>81</sup>.

Results of methylene blue dye sensitized photopolymerization indicate that conditions which perturb the equilibrium between the monomeric and associated forms of the dye

(such as by changing the relative amounts of the monomeric and associated forms by the addition of a doubly charged anionic dye that seldomly associates in solution) influence the polymerization kinetics substantially. Furthermore, chemical substitution on the thiazine nucleus produces wide differences in the sensitizing action of methylene blue; electron donating substituents activate while electron withdrawing substituents deactivate the dye molecule.

Photosensitized polymerization of acrylonitrile by acriflavine in the presence of  $\text{SnCl}_2$  was investigated both in the presence and in the absence of oxygen. It was observed that the presence of oxygen was not critical and it was not at all necessary. A transient Sn-ion of odd valency ( $\text{Sn}^{3+}$  and/or  $\text{Sn}^+$ ), initiating the polymerization by interacting with the monomer, was postulated. Oxygen in fact was observed to exhibit more of an interfering role than of a promoting role in effecting polymerization<sup>82,83</sup>.

In the studies of photopolymerization of aqueous acrylonitrile, a mechanism of the generation of initiating radicals has been suggested by the interaction of the triplet state of methylene blue dye with a benzene sulfinate or a substituted benzene sulfinate ion<sup>84,85</sup>.

#### Dye sensitized solid-state polymerization of acrylamide

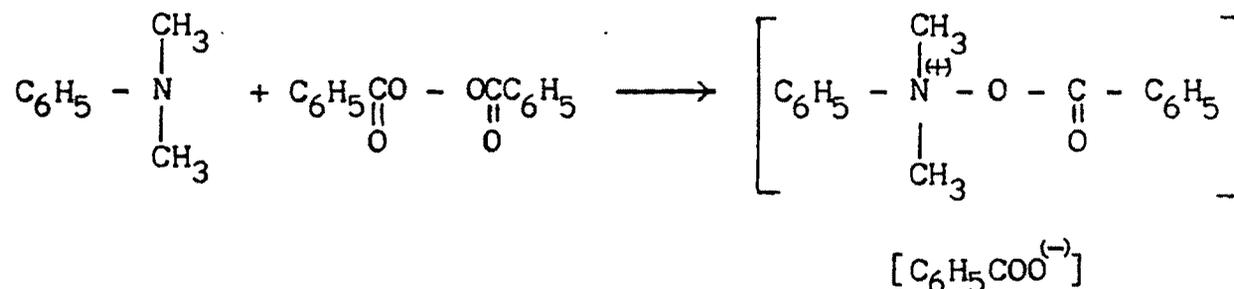
In the solid-state polymerization of acrylamide using methylene blue as a photosensitizer, visible light was found

to be more effective than ionizing radiation. There is evidence that the orientation of the dye in the acrylamide crystal is important<sup>93</sup>. The polymerization has been shown to be initiated by the energy transfer between the activated dye and the monomer<sup>94</sup>.

## 2.2 Peroxide-amine combinations as initiators for vinyl polymerization

A number of organic redox processes are useful initiators in vinyl polymerization in non-aqueous media, one of the best known systems being the amine-peroxide system. Among the different amine-peroxide systems, one that has drawn wide attention in the context of initiation of vinyl polymerization is the benzoyl peroxide ( $Bz_2O_2$ )-N,N dimethylaniline (DMA) combination<sup>121-156</sup>. Reports on the other peroxide-amine initiator systems are also available<sup>157-176</sup>.

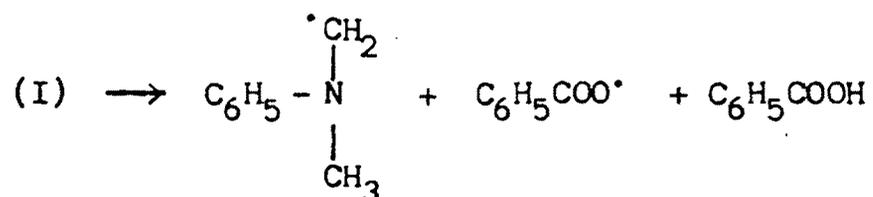
Polymerization of styrene using  $Bz_2O_2$  as initiator is strongly accelerated by low concentrations of DMA and the primary process appears to be the formation of a polar complex (I) between the peroxide and the amine<sup>121-126</sup>.



(I)

7024

and the complex in turn dissociates into radicals as shown below :



The radicals thus generated initiate polymerization<sup>127-131</sup>.

One of the important observations of Horner<sup>121-123</sup> indicated that higher the electron density of the lone pair on the nitrogen atom in substituted DMA, the stronger the promoting effect on the decomposition rate of  $\text{Bz}_2\text{O}_2$ .

Lal<sup>132</sup> observed that substitution of DMA in the para position with electron donating groups enhances the decomposition of  $\text{Bz}_2\text{O}_2$  and accelerates the rate of polymerization whereas similar substitution with electron withdrawing groups decrease the decomposition of  $\text{Bz}_2\text{O}_2$  and retards the rate of polymerization. Aliphatic tertiary amines are much less reactive than aromatic tertiary amines in accelerating the polymerization rate whereas aniline (a primary aromatic amine) and methylaniline (a secondary aromatic amine) act as retarders in the polymerization of styrene by  $\text{Bz}_2\text{O}_2$ .

From a study of the rates of decomposition of  $\text{Bz}_2\text{O}_2$  and substituted  $\text{Bz}_2\text{O}_2$  in the presence of DMA it was confirmed that electron attracting substituents in  $\text{Bz}_2\text{O}_2$  (p-p'-dinitrobenzoyl peroxide or o-o'-dichlorobenzoyl peroxide) accelerated the decomposition and electron donating groups

(p-p'-dimethoxy benzoyl peroxide or p-p' dimethyl benzoyl peroxide) retarded it. As an intermediate reaction of  $Bz_2O_2$  with DMA, a loose complex might be produced by coordination of the electron lone pair in the nitrogen atom with the peroxide central atom and through this intermediate the decomposition might have occurred<sup>133</sup>.

Imoto et al. investigated the effects of different parameters such as concentrations of the initiator components, solvents, temperature, nature and concentration of the monomer etc. on the  $Bz_2O_2$ -DMA initiated polymerization of different vinyl monomers<sup>134-136</sup>.

Tobolsky's theory of "dead-end" polymerization<sup>137</sup> showing that free radical polymerization proceeds only to a limiting conversion has been extended to redox polymerization with  $Bz_2O_2$ -DMA system and soon after mathematical expressions have been developed to describe the course of polymerization showing that free radicals are produced via a second order rate process<sup>138,139</sup>. The dependence of rate of polymerization on the concentration of DMA in DMA- $Bz_2O_2$  initiated vinyl polymerization has been quantitatively explained<sup>140,141</sup> and the catalytic efficiency has been calculated<sup>142</sup> using the "dead-end" theory.

Spectral investigations on the polymerization of vinyl monomers initiated by  $Bz_2O_2$ -DMA combination showed that an initial complex was formed between the initiator components<sup>143-145</sup>.

Studies of polymerization of different vinyl monomers in bulk or in aqueous emulsions using  $Bz_2O_2$ -DMA system showed that the polymerization rates were in the order acrylonitrile > MMA > styrene<sup>146-148</sup>.

Ghosh et al<sup>157</sup> studied photopolymerization of MMA using triethylamine (TEA)- $Bz_2O_2$  system as photoinitiator. Chain initiation was considered to take place through radicals generated by the photo-decomposition of TEA- $Bz_2O_2$  complex formed in situ, the radical generation step being solvent or monomer dependent. Kinetic non-idealities were interpreted in terms of significant initiator dependent termination via degradative chain transfer.

In the studies of emulsion polymerization of styrene initiated by systems containing  $Bz_2O_2$  and a series of water soluble tertiary amines such as  $Et_3N$ , N,N-dimethylamino-ethanol etc., the reaction of  $Bz_2O_2$  with an amine producing free radicals was first order with respect to both peroxide and amine<sup>158,159</sup>.

In the studies of polymerization of MMA using  $Bz_2O_2$ -amine initiator systems, the aromatic tertiary amines showed structural effects on the rate of polymerization. The p-substituted electron donating groups on the ring of the aromatic amine molecules increased the rate of polymerization while the electron withdrawing groups decreased it in the order : N,N-dimethyl p-toluidine > p(hydroxymethyl) N,N dimethyl aniline > N,N dimethyl aniline > p-nitro N,N dimethyl aniline ~ p-dimethyl amino benzaldehyde.

The catalytic activity of various peroxides in the presence of tertiary amines such as dimethyl p-toluidine was found to be in the order benzoyl peroxide > lauroyl peroxide > tert. butyl peroxybenzoate and the diacylperoxide always gave higher rate of bulk polymerization than organic hydroperoxide in the order benzoyl peroxide > lauroyl peroxide > cumene hydroperoxide > tert. butyl hydroperoxide<sup>160-163</sup>.

From the ESR spectral studies of the propagating radicals in the polymerization of MMA using  $Bz_2O_2$ -DMA system as initiator, it has been established that the propagation step is a diffusion control process<sup>164</sup>.

### 2.3 Vinyl polymerization induced by Michler's ketone under photo condition

The usefulness of aromatic ketones as photosensitizers and their effectiveness in inducing photopolymerization of vinyl monomer is well known.

Yokota et al<sup>177</sup> on the other hand studied photopolymerization of methyl methacrylate using certain amines as initiators or sensitizers. Amines, however, are reported to produce inhibition or retardation effects in vinyl polymerization<sup>178,179</sup>. However, amines produce very effective initiator systems particularly under photo activation in the presence of such suitable additives as halomethanes<sup>180-183</sup>, and aromatic ketones such as benzophenone, Fluorenone etc.<sup>184-191</sup> besides their being effectively used in redox combination with peroxides such as  $Bz_2O_2$  as discussed in the preceding sections.

In combination with halomethanes or aromatic ketones the amine contribute to radical generation via complexation between them and the specific additive used under thermal or more commonly under photoconditions. Combinations of amines, acids, acid anhydrides or acid chlorides have also been reported to initiate vinyl photopolymerization through intermediacy of CT-complexes formed between the initiating components<sup>121,145,192-194</sup>.

Michler's ketone which is chemically 4,4'-bis(N,N-dimethyl amino) benzophenone bears the distinction of being an aromatic ketone and amine at the same time and hence it has drawn widespread attention in relation to its use as a photosensitizer and photoinitiator in vinyl polymerization.

A large number of published reports are available on the enhanced light sensitivity of a variety of photocure systems (Photoresists) when Michler's ketone is added to appropriate sensitizers such as benzophenone<sup>195,196</sup> and benzoin alkylether<sup>197</sup>. The technological importance of such initiator combinations is recognized particularly in relation to their use as active ingredients in the field of photocuring of surface coatings and preparation of relief printing plates and printed circuit boards<sup>198-201</sup>.

For MK, the electronic configuration is the main factor in determining its chemical activity. The  $\pi, \pi^*$  configuration of the triplet state exists in addition to n,  $\pi^*$  state. The conjugative interaction of non-bonding electrons of the amino groups with aromatic rings lowers the energy of the



effectively used to induce photopolymerization in combination with some other additives which themselves are good photosensitizers. Use of MK in combination with a peroxide such as benzoyl peroxide for vinyl polymerization under different conditions, thermal or photo, appears to have received little attention so far.

#### 2.4 Main theme of the present thesis

The background knowledge and information and the subsequent detailed literature survey predict that there is ample scope for making further studies on the kinetics and mechanistic of vinyl polymerization thermally or under photoconditions using redox combinations of benzoyl peroxide and certain dyes or dye-intermediates bearing secondary or tertiary amine moieties in their molecule in non-aqueous medium. Keeping this scope and objective in view the author undertook broadbased studies on polymerization of methyl methacrylate (MMA), a vinyl monomer using catalytic concentrations of Rhodamine 6G-anhydrobase (Rh), Auramine O anhydrobase (Au), crystal violet lactone (CVL) and Michler's ketone (MK) in combination with benzoyl peroxide in each case as the initiator systems in separate sets of experiments under photo or thermal conditions.

The general features of the polymerization of MMA using different dye-benzoyl peroxide combinations in various concentrations as initiators in influencing the rates have also been studied and analyzed. Subsequent studies made relate to the kinetics of the polymerization of MMA using

the above initiator combinations in bulk and under diluted conditions with various solvents or diluents which may not or may influence the rates of polymerization to different degrees. The analysis of kinetic data was also made to ascertain if the kinetic non-idealities observed in these systems could also originate at a step subsequent to the initiation step.

Investigations to study and interpret kinetic non-idealities and its degree were also kept within the perview of the objective of the present thesis.

